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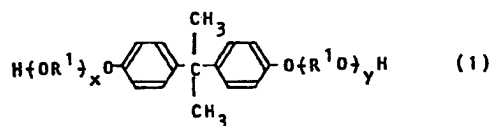
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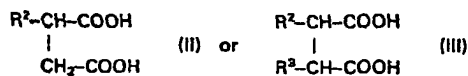
(54) Process for producing new polyester resin.

(57) A new polyester resin is produced by condensation polymerization of (a) a diol component of the formula:



where R² and R³ are saturated or unsaturated hydrocarbon groups of 4 to 20 carbon atoms and 10 to 30 mol% of trimellitic acid or anhydride thereof. The polyester has improved toughness, abrasion resistance and flexibility.

wherein R¹ is an alkylene group of 2 to 4 carbon atoms; and x and y are positive integers, the sum of them being 2 to 16 on an average, and (b) an acid component of polybasic (at least dibasic) carboxylic acid, anhydride thereof, and lower alkyl ester thereof, said acid component (b) containing 1 to 50 mol% of a dibasic carboxylic acid or anhydride thereof of the formula:



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PROCESS FOR PRODUCING NEW POLYESTER RESIN

The present invention relates to a process for producing a new polyester resin which has outstanding toughness, abrasion resistance, and flexibility.

Heretofore, there are known several processes for the production of polyester resins. According to them, linear polyesters are produced by reacting a dicarboxylic acid with a diol having etherified diphenyl nonlinear polyesters are produced by reacting an etherified polyhydroxyl compound as a third component in addition to said two components; and nonlinear polyesters are produced by reacting polybasic (at least tribasic) carboxylic acid as a third component in addition to said two components.

The polyester resins produced by these processes have good performance to some extent, but they still have some disadvantages. For instance, the linear polyester resin is readily soluble in the unsaturated monomer but lacks toughness and abrasion resistance, and consequently it is not necessarily satisfactory in performance as a curing polyester resin. It may be used as a binder for the toner used in electrophotography, but cannot be used for a high-speed copying machine which employs a heat roller for fixation. If it is used for such a copying machine, it will cause off-set.

Nonlinear polyesters, too, have a disadvantage. If an etherified polyhydroxyl compound is used as a third component, the resulting polyester resin improves in toughness

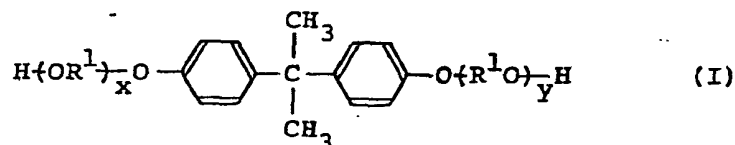
and abrasion resistance, while maintaining the solubility in the unsaturated monomer to some extent. Nevertheless, it does not improve in the glass transition temperature and tends to form a mass when used in the form of powder. On account of these disadvantages, the nonlinear polyester cannot be used as a binder for glass fiber mat and as a binder for the toner used in electrophotography.

Moreover, the nonlinear polyester resin produced by reacting a polybasic (at least tribasic) carboxylic acid
 10 as a third component does not improve in the properties if the acid is used in a small quantity. On the other hand, if the quantity of the acid is increased to produce a good effect, the resulting polyester resin becomes rigid and brittle and rises in the softening point; in addition it is insoluble in the unsaturated monomer. Thus, such a polyester cannot be used as a curing polyester, and it tends to solidify in the reaction vessel during production. This invites a danger in the manufacturing process.

Under these circumstances, there has been a demand for
 20 a polyester resin which is outstanding in toughness and abrasion resistance and soluble in the unsaturated monomer and has a comparatively high glass transition temperature and an adequate softening point.

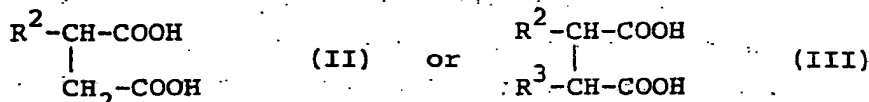
In order to overcome the above disadvantages, the present inventors have carried out a series of researches which led to this invention.

This invention relates to a process for producing a new polyester resin by condensation polymerization of (a) a diol component represented by the formula:



30 (where R^1 is an alkylene group of 2 to 4 carbon atoms; and x and y are positive integers, the sum of them being 2 to 16 on an average), and (b) an acid component selected from the group consisting of polybasic (at least dibasic)

carboxylic acid, anhydride thereof, and lower alkyl ester thereof, said process being characterized by that said acid component (b) contains 1 to 50 mol% of a dibasic carboxylic acid or anhydride thereof represented by the formula:



(where R^2 and R^3 are saturated or unsaturated hydrocarbon groups of 4 to 20 carbon atoms) and 10 to 30 mol% of trimellitic acid or anhydride thereof.

The more is used the trimellitic acid or anhydride thereof, the higher is the glass transition temperature of the resulting resin and the more improves the abrasion resistance of the resulting resin. This improvement is made at the sacrifice of increased rigidity. On the other hand, the more is used the compound or anhydride thereof represented by the formula (II) or (III), the more improves the resulting resin in impact resistance, flexing resistance, and solubility. This improvement is made at the sacrifice of the lowered glass transition temperature and the tendency that the powder of the resin tends to form a mass. These merits and demerits can be balanced if the quantity of the trimellitic acid or anhydride thereof is limited to 10 to 30 mol%, preferably 20 to 30 mol%, in the acid component (b), and the quantity of the compound or anhydride thereof represented by the formula (II) or (III) is limited to 1 to 50 mol% in the acid component (b).

Examples of acid component (b) other than (II) and (III) include phthalic acid, isophthalic acid, terephthalic acid, fumaric acid, maleic acid, anhydrides thereof, and lower alkyl esters thereof, which are used for the production of prevailing polyesters.

The polyester resin produced according to the process of this invention will be used (1) in the form of powder, (2) in the form of a solution dissolved in an organic solvents, and (3) in the form of a solution dissolved in

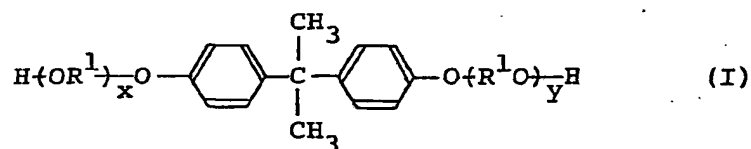
an unsaturated monomer. For application of (3), it is necessary to use fumaric acid or maleic acid, which is an unsaturated dicarboxylic acid, as one of the acid component (b) other than (II) and (III); but for applications of (1) and (2), there is no limitation as to the kind of the acid to be used.

The polyester resin produced according to the process of this invention has a softening point of 80 to 150°C, preferably 100 to 140°C, as measured by the ring and ball method.

The polyester resin produced according to the process of this invention will be used in the form of powder as a binder for glass fiber mat and a binder for electrophotography toner, and in the form of a solution dissolved in an organic solvent as a binder to bond a photoconductive substance to the substrate.

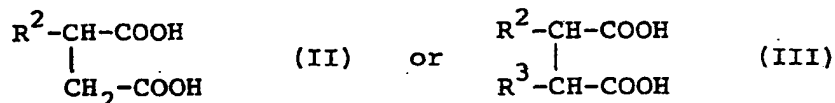
If an unsaturated dicarboxylic acid or anhydride thereof is used as one of the acid component (b), the polyester of this invention will be used as a so-called thermosetting polyester resin after being dissolved in an unsaturated monomer such as styrene, vinyltoluene, chlorostyrene, and diallylphthalate.

Examples of the diol which is used in this invention and is represented by the formula:



(where R^1 , x , and y are as defined above) include polyoxypropylene (2.2)-2,2-bis(4-hydroxyphenyl)propane, polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane, polyoxypropylene(6)-2,2-bis(4-hydroxyphenyl)propane, and polyoxypropylene(16)-2,2-bis(4-hydroxyphenyl)propane.

Examples of the dibasic carboxylic acid which is used in this invention and is represented by the formula:



(where R^2 and R^3 are as defined above)

include n-dodecenylsuccinic acid, iso-dodecenylsuccinic acid, n-dodecylsuccinic acid, iso-dodecylsuccinic acid, iso-octylsuccinic acid, and n-butylsuccinic acid.

The diol component used in this invention may be incorporated with less than about 5 mol% of a polyhydroxyl compound which is at least difunctional.

Examples of such polyhydroxyl compound include ethylene glycol, propylene glycol, glycerin, pentaerythritol, tri-
 10 methylolpropane, hydrogenated bisphenol A, sorbitol, or etherified polyhydroxyl compound thereof such as polyoxy-ethylene(10) sorbitol, polyoxypropylene(3) glycerin, and polyoxyethylene(4) pentaerythritol.

According to the process of this invention, the polyester resin can be produced by polycondensing the polyol component and the polybasic carboxylic acid at 180 to 250°C in an inert gas atmosphere. In order to accelerate the reaction, a common esterification catalyst such as zinc oxide, stannous oxide, dibutyltin oxide, and dibutyltin di-
 20 laurate can be used. Also, the process can be carried out under a reduced pressure for accelerated reaction.

The invention will be illustrated by the following non-limitative examples for the production and use of the resin.

Production Example 1

Into a 1-liter 4-neck glass flask equipped with a thermometer, stainless steel stirrer, condenser, and nitrogen inlet were charged 700 g of polyoxypropylene(2.2)-2,2-bis-(4-hydroxyphenyl)propane, 130 g of fumaric acid, 53.4 g of n-dodecenylsuccinic anhydride, and 0.1 g of hydroquinone.
 30 Using an electric mantle heater, the reactants were heated to 230°C, with stirring under a nitrogen stream, until the water formed by reaction was not distilled out any longer. The acid value at that time was 1.5.

Subsequently, 63.4 g of trimellitic anhydride was added and reaction was continued for about 8 hours until the acid value reached 20. A light yellow solid resin having a ring and ball softening point of 120°C was obtained.

Comparative Example 1

10 Into the same apparatus as used in Example 1 were charged 700 g of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane, 333 g of fumaric acid, and 0.1 g of hydroquinone. Reaction was continued at 220°C with stirring under a nitrogen stream, until the acid value reached 20. A light yellow solid resin having a ring and ball softening point of 108°C was obtained.

Comparative Example 2

Into the same apparatus as used in Example 1 were charged 700 g of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane, 153 g of fumaric acid, and 0.1 g of hydroquinone. Reaction was continued until the water formed by reaction was not distilled out any longer. The acid value at that time was 1.8.

20 Subsequently, 63.4 g of trimellitic anhydride was added and reaction was continued for about 8 hours until the acid value reached 20. A light yellow solid resin having a ring and ball softening point of 125°C was obtained.

Usage Example 1

The resin obtained in Production Example 1 was incorporated with 65 wt% of styrene. The resulting clear polyester monomer solution was incorporated with benzoyl peroxide and then applied to a glass fiber mat. After curing at 90°C for about 1 hour, an inflexible glass fiber laminate was obtained.

30 On the other hand, the resin obtained in Comparative Example 1 was incorporated with 65 wt% of styrene. The resulting turbid solution was applied to a glass fiber mat in the same manner as above. The resulting glass fiber laminate caused whitening and cracking when bent.

The resin obtained in Comparative Example 2 was not dissolved in 65 wt.% of styrene completely. Thus, the resulting solution was not suitable for production of glass fiber laminate.

Production Example 2

Using the same apparatus as used in Production Example 1,

650 g of polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane, 120 g of fumaric acid, and 53.4 g of iso-dodecenylsuccinic anhydride were reacted at 220°C, until the water formed by reaction was not distilled out any longer. The acid value at that time was 1.3.

Subsequently, 79 g of trimellitic anhydride was added and reaction was continued at 200°C until the ring and ball softening point reached 120°C. After standing for cooling and solidifying, the resin was crushed into powder which
10 passes 42 mesh (350 µm opening) and contains more than 80% of the fraction which passes 42 mesh (350 µm opening) and remains on 150 mesh (100 µm opening).

Comparative Example 3

Using the same apparatus as used in Production Example 1, 617 g of polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane, 232 g of fumaric acid, and 9 g of glycerin were reacted at 220°C, until the ring and ball softening point reached 120°C. After standing for cooling and solidifying, the resin was crushed into powder which passes 42 mesh and contains
20 more than 80% of the fraction which passes 42 mesh and remains on 150 mesh.

Usage Example 2

A glass fiber mat was produced as follows using as a binder the resin powder obtained in Production Example 2.

The first glass fiber layer was prepared by spreading uniformly chopped glass strand on a perforated steel plate measuring 35 cm by 35 cm placed in a mat producing test machine equipped with a blower. Water was sprayed for 10 seconds. With the blower stopped, the powder binder was
30 spread uniformly on the mat. These steps were repeated four times to prepare a four-layered glass fiber mat. The mat was heated in an oven at 200°C for 10 minutes. The quantity of the powder binder was controlled so that the final loading is 3 to 4 wt% based on the glass fiber. On removal from the oven, the glass fiber mat was cooled immediately by putting between two steel plates. After cooling, the mat was cut to a size of 10 cm by 25 cm, and this

test piece was measured for tensile strength on an autographic tensile tester (made by Shimadzu Seisakusho).

On the other hand, the powder binder was evaluated for caking by calculating the caking index as follows:

The resin powder prepared in Production Example 2 was vacuum dried at normal temperature for 2 days. Exactly 12 g of this powder was placed in a 40 cc beaker, and allowed to stand in the atmosphere of 35°C and 40% RH, 70% RH and 100% RH for 2 days. The conditioned powder was kept pressed under a load of 200 g for 1 week. After removal of the load, the powder was taken out of the beaker slowly so as not to break the shape. The lump of the powder was dropped on a 20 mesh screen from a height of 50 cm. After slight shaking of the screen, the quantity of the powder remaining on the screen was measured. Let the weight W g, and the caking index is given by the following expression.

$$\text{Caking index} = W \times 100/12$$

The resin prepared in Comparative Example 3 and a commercial binder resin having the same particle size as that resin were evaluated for caking index, and the glass fiber mats produced from them were measured for tensile strength in the same manner as above. (The commercial binder resin is Atlack 363E (made by Kao Atlas), having an acid value 15 and a ring and ball softening point 112°C, made from polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane and fumaric acid. The results are shown in Table 1.

Table 1

	Mat tensile strength (kg)	Caking Index		
		35°C, 40% RH	35°C, 70% RH	35°C, 100% TH
Resin powder of Product. Ex. 2	18.0	0	0	5
Resin powder of Comp. Ex. 3	15.5	0	55	85
Atlack 363E resin powder	15.0	0	45	75

Table 1 indicates that the resin powder obtained in Production Example 2 is superior in mat tensile strength and is more resistant to caking.

Production Example 3-1

Using the same apparatus as used in Production Example 1, 490 g of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)-propane, 195 g of polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane, 188 g of terephthalic acid, 26.8 g of n-dodecyl-succinic anhydride, and 0.8 g of diisopropyl ortho-
10 titanate as an esterification catalyst were reacted at 230°C for about 5 hours until the acid value reached 2.0.

Subsequently, 78.8 g of trimellitic anhydride was added . are reaction was continued at 200°C for about 4 hours under reduced pressure until the ring and ball softening point reached 115°C. A light yellow solid resin having an acid value of 33 was obtained.

Production Example 3-2

In the same manner as Production Example 3-1, a resin having a softening point of 120°C was obtained. Those resins
20 obtained in Production Examples 3-1 and 3-2 were soluble in organic solvents such as dioxane and methyl ethyl ketone.

Comparative Example 4-1

Using the same apparatus as used in Production Example 1, 490 g of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)-propane, 195 g of polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)-propane, 204.3 g of terephthalic acid, and 0.8 g of diisopropyl orthotitanate were reacted at 230°C for about 5
30 hours. Subsequently, 78.8 g of trimellitic anhydride was added and reaction was continued at 200°C for about 4 hours under reduced pressure until the ring and ball softening point reached 115°C. A light yellow solid resin having an acid value of 34 was obtained.

Comparative Example 4-2

Comparative Example 4-1 was repeated except that the reaction was continued until the softening point reached 120°C.

Comparative Example 4-3

Comparative Example 4-1 was repeated except that the reaction was continued until the softening point reached 125°C.

Comparative Example 5-1

Using the same apparatus as used in Production Example 1, 490 g of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)-propane, 195 g of polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane, 97 g of terephthalic acid, and 0.8 g of diisopropyl orthotitanate were reacted at 230°C for about 5 hours. The acid value was 1.8. Subsequently, 156 g of trimellitic anhydride was added and reaction was continued at 200°C for about 5 hours until the ring and ball softening point reached 120°C. The resulting light yellow solid resin was insoluble in all the solvents tested, and it was very difficult to clean the reaction apparatus.

Comparative Example 5-2

Comparative Example 5-1 was repeated except that the reaction was continued until the softening point reached 125°C. The resulting light yellow solid resin was insoluble in all the solvents tested, and it was very difficult to clean the reaction apparatus.

In both Comparative Examples 5-1 and 5-2, the polymerization rate was so high that there was a danger that the resin solidifies in the reaction apparatus.

Usage Example 3

An electrophotography toner was prepared as follows. Ninety-five parts of the resin obtained in Production Example 3-1 was mixed with 5 parts of carbon black in a ball mill, and then kneaded by a hot roll. After cooling and solidifying, the resin mixture was crushed by a hammer and then by a jet mill into fine powder having an average particle size of about 15 microns.

In the same manner as above, fine powders of the same particle size were prepared from the resins obtained in Production Example 3-2 and Comparative Examples 4-1 to 5-2.

Five grams each of the black fine powders was mixed with

95 g of iron powder of 150 to 200 mesh to make electrophotography toners. The toners were evaluated for the quality of images and off-set by applying by the magnetic brush method. The results are shown in Table 2.

Table 2

<u>Resins</u>	<u>Ring and ball softening point (°C)</u>	<u>Off-set</u>	<u>Quality of image</u>
Resin of Prod. Ex. 3-1	115	No	Good
Resin of Prod. Ex. 3-2	120	No	Good
Resin of Comp. Ex. 4-1	115	Yes	Blurred
Resin of Comp. Ex. 4-2	120	Yes	Good
Resin of Comp. Ex. 4-3	125	No	Poor fix
Resin of Comp. Ex. 5-1	120	Yes	Good
Resin of Comp. Ex. 5-2	125	No	Poor fix

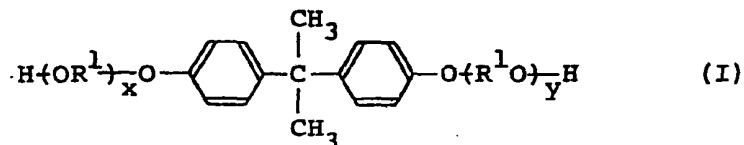
Table 2 indicates that the toners prepared from the resins obtained in Production Examples 3-1 and 3-2 gave good images without causing off-set even in the case of the resin having a lower softening point.

10 In contrast, the resins obtained in Comparative Examples 4-1 to 4-3 caused off-set except the resin having the highest softening point which is poor in fixation. This is also true in the case of the resins obtained in Comparative Examples 5-1 and 5-2. As mentioned above, these resins are more difficult to produce than the resin of this invention.

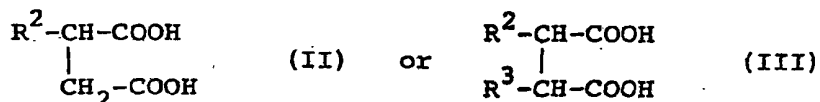
What is claimed is:

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A process for producing a new polyester resin by condensation polymerization of (a) a diol component represented by the formula:



(where R^1 is an alkylene group of 2 to 4 carbon atoms; and x and y are positive integers, the sum of them being 2 to 16 on an average), and (b) an acid component selected from the group consisting of polybasic (at least dibasic) carboxylic acid, anhydride thereof, and lower alkyl ester thereof, said process being characterized by that said acid
 10 component (b) contains 1 to 50 mol% of a dibasic carboxylic acid or anhydride thereof represented by the formula:



(where R^2 and R^3 are saturated or unsaturated hydrocarbon groups of 4 to 20 carbon atoms) and 10 to 30 mol% of trimellitic acid or anhydride thereof.

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A process as claimed in Claim 1, wherein said dibasic carboxylic acid of the formula (II) or (III) is selected from the group consisting of n-dodecenylsuccinic acid, iso-dodecenylsuccinic acid, n-dodecylsuccinic acid, iso-dodecylsuccinic acid, iso-octylsuccinic acid, and n-butylsuccinic acid.

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A process as claimed in Claim 1, wherein said condensation polymerization is conducted at 180 to 250°C in the inert gas atmosphere, in the presence of an esterification catalyst.



European Patent
Office

EUROPEAN SEARCH REPORT

0055449

Application number

EP 81 11 0649.1

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
Y	DE - A1 - 2 402 841 (MEHNERT & VEECK KG) * claims 1, 7 to 9; page 3, line 19 to page 5, line 19 *	1	C 08 G 63/66
Y	BE - A - 625 671 (ATLAS CHEMICAL INDUSTRIES) * claims 1, 4, 8, 10, 12 *	1,3	
Y	GB - A - 2 039 928 (KAO SOAP CO. LTD.) * claims 1, 4; page 1, lines 49 to 60; page 2, lines 7 to 10 *	1,3	TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
A	DE - A - 1 929 070 (GOODYEAR TIRE & RUBBER CO.) * claim 1; page 3, line 27 to page 6, line 12 *	2	C 08 C 53/66 C 09 D 5/40
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search Berlin		Date of completion of the search 24-03-1982	Examiner IDEZ